



**Luminescent article with protective coating and manufacture.**

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 EP0209358**Abstract of EP0510754**

A luminescent article is provided which luminescent article comprises a self-supporting or supported layer of phosphor particles dispersed in a resin binder having applied thereto a protective coating, which has a layer thickness  $d$  comprised between 1 and 50  $\mu\text{m}$ , and an embossed surface roughness  $R_z$  so that the ratio between roughness  $R_z$  and thickness  $d$  is at least 0.35.

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## **Luminescent article with protective coating and manufacture.**

### **Description of EP0510754**

#### **1. Field of the invention.**

The present invention relates to a luminescent article comprising a coating of phosphor particles and a protective coating applied thereto.

#### **2. Background of the invention**

In radiography the interior of objects is reproduced by means of penetrating radiation which is high energy radiation belonging to the class of X-rays, Gamma rays and high energy elementary particle radiation, e.g. Beta-rays, electron beam or neutron radiation. For the conversion of penetrating radiation into visible light and/or ultraviolet radiation luminescent substances are used called phosphors.

In a conventional radiographic system an X-ray radiograph is obtained by X-rays transmitted imagewise through an object and converted into light of corresponding intensity in a so-called intensifying screen (X-ray conversion screen) wherein phosphor particles absorb the transmitted X-rays and convert them into visible light and/or ultraviolet radiation whereto a photographic film is more sensitive than to the direct impact of the X-rays.

In practice the light emitted imagewise by said screen irradiates a contacting photographic silver halide emulsion layer film which after exposure is developed to form therein a silver image in conformity with the X-ray image.

For use in common medical radiography the X-ray film comprises a transparant film support double-side coated with a silver halide emulsion layer. During the X-ray irradiation said film is arranged in a cassette between two X-ray conversion screens each of them making contact with their corresponding silver halide emulsion layer.

Single side coated silver halide emulsion films combined in contact with only one screen are often used in autoradiography, in applications where improved image definition is of great importance e.g. in mammography and in particular fields of non-destructive testing (NDT) known as industrial radiography. An autoradiograph is a photographic record formed through the intermediary of penetrating radiation emitted by radioactive material contained in an object. e.g. microtome cut for biochemical research.

Phosphors suitable for use in the conventional radiographic system must have a high prompt emission on X-ray irradiation and low after-glow in favour of image-sharpness.

More recently an X-ray recording system has been developed wherein photostimulable storage phosphors are used that in addition to their immediate light emission (prompt emission) on X-ray irradiation, have the property to store temporarily a large part of the energy of the X-ray image which energy is set free by photostimulation in the form of light different in wavelength characteristic from the light used in the photostimulation. In said X-ray recording system the light emitted on photostimulation is detected photo-electronically and transformed in sequential electrical signals.

The basic constituents of such X-ray imaging system operating with storage phosphors are an imaging sensor containing said phosphor, normally a plate or panel, which temporarily stores the X-ray energy pattern, a scanning laser beam for photostimulation, a photo-electronic light detector providing analog signals that are converted subsequently into digital time-series signals, normally a digital image processor which manipulates the image digitally, a signal recorder, e.g. magnetic disk or tape, and an image recorder for modulated light-exposure of a photographic film or an electronic signal display unit, e.g. cathode ray tube.

From the preceding description of said two X-ray recording systems operating with X-ray conversion phosphor screens in the form of a plate or panel it is clear that said plates or panels serve only as intermediate imaging elements and do not form the final record. The final image is made or reproduced on a separate recording medium or display. The phosphor plates or sheets can be repeatedly re-used. Before re-use of the photostimulable phosphor panels or sheets a residual energy pattern is erased by flooding with light. The expected life of the plate is limited mainly by mechanical damage such as scratches.

Both types of X-ray conversion screens generally comprise in order : a support, a layer comprising phosphor particles dispersed in a suitable binder and a protective coating coated over the phosphor containing layer to protect said layer during use.

Since in the above described X-ray recording systems the X-ray conversion screens are used repeatedly, it is important to provide them with an adequate topcoat for protecting the phosphor containing layer from mechanical and chemical damage.

The protective layer preferably has a relief structure that reduces friction as well as the tendency to show sticking phenomena with contacting materials. The relief structure thus favours loading and unloading of a film from a cassette and reduces the building up of static electricity. Especially in automated loading for daylight systems as e.g. CURIX CAPACITY, an Agfa-Gevaert trade-marked product, the reduction of the building up of static electricity as a consequence of friction phenomena during cassette loading and unloading is a function of the contact area and the distance between both the screens and the photographic film. Once the cassette has been loaded the contact between the film and the screens, necessary to obtain good image quality, is intensified by the application of pressure forces at the cassette surface. As a consequence the air included between the surfaces of the screens and the film escapes and a vacuum is created in the cassette. Sticking phenomena, resulting from said contact have to be avoided whereas the breaking of the vacuum has to be promoted after exposure, when the cassette has to be opened and the film has to be transported to the processing unit. Therefore solid particles can be incorporated that protrude from the protective coating as described e.g. in US Patent 4.059.768.

However, providing a relief structure that effectively improves manipulation as set forth above is at the cost of image quality. Indeed providing protruding particles requires increased thickness of the protective coating and as a consequence reduced image sharpness due to an increased distance between the radiation emitting phosphor layer and the radiation sensitive coating of the photographic film in contact therewith.

Not only the increased thickness itself can give rise to increased unsharpness of the emitted light when the refractive indices of phosphor binder and binder of the protective coating differ but also the presence of the particles themselves having different refractive index compared with that of the binder of the protective coating.

The terminology X-ray conversion screen and phosphor as used herein refers to screens and phosphors for use in conventional screen-film combinations as well as for stimulated luminescence radiography. In the latter case improved manipulation, especially transport of the screen is required as the screen itself has to be transported from the exposure site to the unit where it has to be read out by stimulating light.

Roughening the protective layer by addition before coating of solid particles, e.g. polystyrene beads with a diameter of e.g. 25  $\mu\text{m}$  promotes the transport characteristics of said layer but has a disadvantageous effect on abrasion resistance as these particles will be worn off. In addition the thickness of the protective layer changes together with the roughness factor and strongly depends on the viscosity of the layer which is differing as a function of the solvents used, the coating temperature and the drying conditions, being directly responsible for the penetrating depth of the particles e.g. polystyrene beads in the coated layer. As a consequence the really measured thickness depends on the amount of protrusion of said particles.

### 3. Objects of the invention

It is an object of the present invention to provide a luminescent article, e.g. in the form of a plate, panel or web, comprising a phosphor-binder layer and protective coating applied thereto the protective layer having a relief structure for high ease of manipulation; thereby avoiding sticking, friction and electrostatic

attraction with maintenance of an excellent image resolution.

Other objects and advantages of the invention will become clear from the following description and examples.

#### 4. Summary of the invention.

In accordance with the present invention a luminescent article is provided which luminescent article comprises a self-supporting or supported layer of phosphor particles dispersed in a resin binder having applied thereto a protective coating having an embossed structure, more particularly a protective coating having a layer thickness  $d$  comprised between 1 and 50  $\mu\text{m}$  and having an embossed surface roughness  $R_z$  so that the ratio between roughness  $R_z$  and thickness  $d$  is at least 0.35.

The embossed protective layer can be provided on the phosphor layer in order to protect it against mechanical and chemical damage by the steps of

- (1) coating onto said phosphor containing layer a liquid radiation-curable composition having at the coating temperature a viscosity of at least 450 mPa.s, measured with a Hoeppler viscometer, that does not penetrate for a substantial degree into the phosphor containing layer,
- (2) providing an embossed structure to the coating, and
- (3) curing said coating by radiation.

#### 5. Detailed description of the invention

The correlating features of roughness and thickness of the protective coating confer to the screen of the present invention desirable and unexpected properties of ease of manipulation and excellent image sharpness.

The thickness  $d$  of a protective layer of the phosphor screen formed according to the present invention is in the range from 1 to 50  $\mu\text{m}$ , preferably from 2 to 30  $\mu\text{m}$  and more preferably from 3 to 25  $\mu\text{m}$  whereby a very flexible and sufficiently abrasion-resistant coating is obtained.

Whereas the thickness of the protective layer can be measured from microscopic intersections or with a thickness measuring apparatus on microscale, roughness  $R_z$  has to be determined as the arithmetic mean roughness depth value  $R_t$  of five different, but subsequent measuring area; said value  $R_t$  being defined as the difference in height between the highest "top" and the lowest "valley". A suitable instrument for such microscopically fine measurements is a "perthometer", by means of which the surface texture can be measured according to ANSI B46.1-1985 as published by The American Society of Mechanical Engineers.

The value of  $R_z$  for a layer thickness  $d$  of about 8  $\mu\text{m}$  with which favourable image sharpness is obtained, should be at least 3.0  $\mu\text{m}$  to reach a value of the ratio between both parameters of at least 0.35, this value being called  $VR_d$  and thus being represented by the expression  $VR_d = R_z : d$ .

The roughness of the topcoat layer of an intensifying screen offers the advantage that sticking phenomena between a film and an intensifying screen(s) in a cassette are substantially avoided even after intimate contact due to pressure build-up in the cassette system.

In relation to transport characteristics of a film in a cassette the use of an X-ray conversion phosphor screen having a topcoat with embossed structure favours its practically frictionless loading and unloading of a cassette and reduces considerably the built up of static electricity. The micro-channels formed by the embossed structure of the protective coating allow air to escape between phosphor screen and contacting film whereby image quality (image sharpness) is improved by better screen-film-screen contact without large air bubble inclusions.

According to a preferred embodiment the coating of the protective layer proceeds by screen-printing (silk-screen printing).

The screen printing process is preferred for applying paste-consistency coating compositions (viscosity at least 1000 mPa.s at coating temperature) in a fairly small thickness, e.g. coating thickness in the range of 2 to 15  $\mu\text{m}$ .

Particulars about screen printing with hand-operated, automatic and semi-automatic presses can be found in the following literature:

"The Complete Book of Silk Screen Printing Production" by J.I. Biegeleisen - Dover Publications, Inc. New York (1963) and in "Printing Technology" 3rd Edition by J. Michael Adams et al., - Delmar Publishers Inc. USA, (1988), p. 431-445. The standard screen printing device comprises a screen printing frame wherein a piece of fabric or sieve is stretched. For printing (not for simple coating purposes) the sieve is blocked image-wise and forms a stencil. A flexible squeegee is used to force the ink (here the radiation-curable coating composition) through the sieve openings to reach the substrate whereon the ink or coating composition is deposited and after separation from the sieve is dried or hardened.

In a preferred embodiment the protective coating composition is applied by a rotary screen printing device as has been described in detail in European Patent Application 91201009.7 filed April 26, 1991. In said document such device is illustrated schematically by the accompanying drawing.

The rotary screen printing device operating as coating device applies a paste-like consistency coating composition through a seamless rotary screen in the form of a sleeve. A flexible squeegee blade (made from stainless steel) adjustably arranged in a clamp presses the paste through the perforated screen wall of the screen on the substrate. According to the present invention the substrate is e.g. a film support having coated thereto a phosphor-binder layer. The web-type substrate is guided by a counter pressure roller. The paste-like coating composition is fed through the distribution pipe arranged inside the rotary screen which at its sleeve ends is secured to ring members freely rotating in ball bearings. The screen is pneumatically tensioned in its axial direction. A pump and level control means guarantee a constant paste supply. As known to those skilled in the art thin-walled screens can be made by weaving using natural or synthetic polymer yarns or fine metal wire. According to another technique the screen is made by electro-deposition of metal, e.g. nickel, in a screenlike pattern.

It has been found that screens having a screen fineness of 10 to 500 lines/cm and an open area percentage (permeability percentage) with respect to the total screen surface in the range of 5-45 % give satisfactory coating results with radiation-curable liquid coating compositions having a viscosity in the range of 1000 to 5000 mPa.s, the viscosity being lower in the case of a finer opening structure of the screen. The thickness of the sieve or screen can be between 50 and 150 micron, preferably is about 100 micron. Particularly smooth, thin flexible protective coatings can be prepared by the use of a screen printing device operating with screens having a thickness in the range of 10-110  $\mu\text{m}$ , 3000 to 4500 holes per  $\text{cm}^2$  and hole diameter of 80 to 40  $\mu\text{m}$ .

Particularly useful high viscosity liquid radiation-curable coating compositions are prepared by means of addition polymerizable liquid prepolymers and/or chemically inert polymers dissolved in addition polymerizable liquid monomers up to the desired viscosity for use according to the present invention.

Very useful radiation curable compositions for forming a protective coating contain as primary components :

- (1) a crosslinkable prepolymer or oligomer,
- (2) a reactive diluent monomer, and in the case of an UV curable formulation
- (3) a photoinitiator.

The usual amounts of these primary components calculated on the total coating composition are 30-100 % by weight for the prepolymer, 10-70 % by weight for the reactive diluent and 0-10 % by weight for the photoinitiator. Optionally minor amounts (e.g. 5 % by weight) of non-reactive organic solvent for the prepolymer may be present.

Examples of suitable prepolymers for use in a radiation-curable composition applied according to the present invention are the following :

unsaturated polyesters, e.g. polyester acrylates; urethane modified unsaturated polyesters, e.g. urethane-polyester acrylates. Liquid polyesters having an acrylic group as a terminal group, e.g. saturated copolyesters which have been provided with acryltype end groups are described in published EP-A 0 207 257 and Radiat. Phys. Chem., Vol. 33, No. 5, 443-450 (1989). The latter liquid copolyesters are

substantially free from low molecular weight, unsaturated monomers and other volatile substances and are of very low toxicity (ref. the journal *Adhäsion* 1990 Heft 12, page 12). The preparation of a large variety of radiation-curable acrylic polyesters is given in German Offenlegungsschrift No. 2838691. Mixtures of two or more of said prepolymers may be used. A survey of UV-curable coating compositions is given e.g. in the journal "Coating" 9/88, p. 348-353.

Other abrasion-resistant topcoats can be obtained by the use of prepolymers also called oligomers of the class of aliphatic and aromatic polyester-urethane acrylates. The structure of polyester-urethane acrylates is given in the booklet "Radiation Cured Coatings" by John R. Constanza, A.P. Silveri and Joseph A. Vona, published by Federation of Societies for Coatings Technology, 1315 Walnut St. Philadelphia, PA 19107 USA (June 1986) p. 9.

The structure of particularly useful aromatic polyester-urethane acrylate prepolymers is illustrated by the following general formula : EMI7.1 wherein R is a C2 to C6 alkylene group.

In the synthesis of said aromatic urethane first tolylene 2,4-diisocyanate is used in a polyaddition reaction with aliphatic diols and the polymerizable double bond end structures are introduced by reaction of terminal isocyanate groups with 2-hydroxyethyl acrylate. In the synthesis of aliphatic urethane acrylates an alkylene diisocyanate is used, e.g. 1,6-diisocyanatohexane.

Examples of the preparation of aliphatic polyester-urethane acrylates, are given in US-P 4,983,505 and in DE 2530896.

The introduction of a plurality of acrylic double bonds per polymer chain of the prepolymer proceeds by first effecting a partial esterification of a polyol, e.g. pentaerythritol, with acrylic acid and a subsequent reaction of the still free HO-group(s) of the polyol with a polyfunctional isocyanate.

Examples of free radical polymerizable liquid monomers that preferably serve as solvent for the prepolymers and therefore are called diluent monomers are the following : methyl (metha)acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, n-hexyl acrylate, lauryl acrylate, tetrahydrofurfurylmethacrylate and the like.

Mono-functional diluent monomers are not necessarily applied in conjunction with unsaturated prepolymers but can be used to form a radiation-curable composition with good abrasion resistance in conjunction with saturated polyesters, e.g. polyethylene terephthalate and polyethylene isophthalate. Preferred mono-functional monomers for use therewith are methyl methacrylate and tetrahydrofurfuryl methacrylate.

Examples of suitable di-functional monomers are : 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, silicone diacrylate, neopentylglycol, 1,4-butanediol diacrylate, ethyleneglycol diacrylate, polyethyleneglycol diacrylate, pentaerythritol diacrylate, divinylbenzene.

A difunctional acrylate e.g. hexane diol diacrylate is preferably used as reactive diluent in an amount of between 0 and 80 % by weight, preferably between 10 and 30 % by weight.

Examples of suitable tri- or more-functional monomers are : trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, dipentaerythritol hexaacrylate, an acrylate of ethylenediamine, aliphatic and aromatic urethane acrylates and the monomers according to general formula (I) described in European patent application No. 91200468.6 filed March 5, 1991, wherein reference is made for the preparation of said monomers to published German patent applications Nos. 3,522,005, 3,703,080, 3,643.216, 3,703.130, 3,703,080, 3,917.320 and 3,743,728.

When the radiation-curing is carried out with ultraviolet radiation (UV), a photoinitiator is present in the coating composition to serve as a catalyst to initiate the polymerization of the monomers and their optional cross-linking with the pre-polymers resulting in curing of the coated protective layer composition.

A photosensitizer for accelerating the effect of the photoinitiator may be present.

Photoinitiators suitable for use in UV-curable coating compositions belong to the class of organic carbonyl compounds, for example, benzoin ether series compounds such as benzoin isopropyl, isobutylether;

benzil ketal series compounds; ketoxime esters; benzophenone series compounds such as benzophenone, o-benzoylmethylbenzoate; acetophenone series compounds such as acetophenone, trichloroacetophenone, 1,1-dichloroacetophenone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone; thioxanthone series compounds such as 2-chlorothioxanthone, 2-ethylthioxanthone; and compounds such as 2-hydroxy-2-methylpropiophenone, 2-hydroxy-4'-isopropyl-2-methylpropiophenone, 1-hydroxycyclohexylphenylketone; etc.

A particularly preferred photoinitiator is 2-hydroxy-2-methyl-1-phenyl-propan-1-one which product is marketed by E. Merck, Darmstadt, Germany under the tradename DAROCUR 1173.

The above mentioned photopolymerization initiators may be used alone or as a mixture of two or more.

Examples of suitable photosensitizers are particular aromatic amino compounds as described e.g. in GB-P 1,314,556, 1,486,911. US-P 4,255,513 and merocyanine and carbostyryl compounds as described in US-P 4,282,309.

To the radiation-curable coating composition there may be added a storage stabilizer, a colorant, and other additives, and then dissolved or dispersed therein to prepare the coating liquid for the protective layer. Examples of colorants that can be used in the protective layer include MAKRAOLEX ROT EG, MAKRAOLEX ROT GS and MAKRAOLEX ROT E2G. MAKRAOLEX is a registered tradename of Bayer AG, Leverkusen, Germany.

When using ultraviolet radiation as curing source the photoinitiator which needs to be added to the coating solution will to a more or less extent also absorb the light emitted by the phosphor thereby impairing the sensitivity of the radiographic screen, particularly when a phosphor emitting UV or blue light is used. In case of use of a green emitting phosphor a photoinitiator has to be chosen of which the absorption range overlaps to a minimum degree with the emission range of the phosphor; a preferred photoinitiator is then DAROCUR 1173 (tradename).

The amount of the photoinitiator used is preferably within the range of 0.01 to 5 parts by weight relative to 100 parts by weight of the prepolymer. In particular, the photoinitiator is preferably used in an amount of 0.5 to 3 parts by weight and within the range of 3 to 7 times the amount of the radical-generating compound used.

The protective coating of the present luminescent article is given an embossed structure following the coating stage by passing the uncured or slightly cured coating through the nip of pressure rollers wherein the roller contacting said coating has a micro-relief structure, e.g. giving the coating an embossed structure so as to obtain relief parts having a height so that the ratio between roughness and thickness is at least 0.35. A suitable process for forming a textured structure in a plastic coating by means of engraved chill roll is described in US-P 3,959,546.

According to another embodiment the textured or embossed structure is obtained already in the coating stage by applying the paste-like coating composition with a gravure roller or screen printing device operating with a radiation-curable liquid coating composition the Hoeppler-viscosity of which at a coating temperature of 25 DEG C is between 450 and 20,000 mPa.s.

The instrument known as Hoeppler viscometer and its use for determining the viscosity of the radiation-curable coating composition applied according to the present invention is described in the book "Viscosity and Flow Measurement - A Laboratory Handbook of Rheology - by J.R. Van Wazer, J.W. Lyons, K.Y. Kim, and R.E. Colwell (Monsanto Chemical Company St. Louis, Missouri (1963) Interscience Publishers a division of John Wiley & Sons. New York - London, p. 276-279. Note that 1 mPa.s = 1 centipoise.

To avoid flattening of the embossed structure under the influence of gravitation, viscosity and surface shear the radiation-curing is effected immediately or almost immediately after the application of the liquid coating. The rheologic behaviour or flow characteristics of the radiation-curable coating composition can be controlled by means of so-called flowing agents. For that purpose alkylacrylate ester copolymers containing lower alkyl (C1-C2) and higher alkyl (C6-C18) ester groups can be used as shear controlling agents lowering the viscosity. The addition of pigments such as colloidal silica raises the viscosity.

A variety of other optional compounds can be included in the radiation-curable coating composition of the present radiographic article such as compounds to reduce static electrical charge accumulation,

plasticizers, matting agents, lubricants, defoamers and the like as has been described in the European Patent Application 91/201009.7. In said document a description has also been given of the apparatus and methods for curing, as well as a non-limitative survey of X-ray conversion screen phosphors, of photostimulable phosphors and of binders of the phosphor containing layer.

The thickness of the phosphor layer, which may differ depending on the sensitivity of the radiographic screen to radiation, the kind of the phosphor, etc., may be within the range of from 10 to 1000 micron, preferably from 50 to 500 micron, more preferably from 150 to 250 micron.

Two or more phosphor layers with different thickness and/or different binder:phosphor ratio and/or different phosphor particle size may be used.

Radiographic screens in particular those comprising conventional non-stimulable phosphors as described above can also be in the form of gradual screens, i.e. screens having a gradual intensification along their length and/or width. Graduality can be achieved by gradually increasing the thickness of the phosphor layer over the length or width of the screen or by incorporating into the protective layer or into an interlayer between the protective layer and phosphor containing layer a gradually increasing amount of dye capable of absorbing the light emitted by the phosphor. According to another convenient technique graduality is obtained by halftone printing of a dye or ink composition absorbing the light emitted by the screen. By varying the screen dot size in the halftone print, i.e. by gradually varying the percent dot area over the length or width of the screen graduality can be obtained in any degree. The halftone printing can proceed on the phosphor containing layer which thereupon is covered with the protective coating or proceeds by applying the protective coating by halftone printing. e.g. by gravure roller or silk screen printing.

Examples of the support material, this survey being non-limitative, include cardboard, plastic films such as films of cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, polystyrene, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate and polycarbonate; metal sheets such as aluminum foil and aluminum alloy foil; ordinary papers; baryta paper; resin-coated papers; pigment papers containing titanium dioxide or the like; and papers sized with polyvinyl alcohol or the like. A plastic film is preferably employed as the support material.

The plastic film may contain a light-absorbing material such as carbon black, or may contain a light-reflecting material such as titanium dioxide or barium sulfate. The former is appropriate for preparing a high-resolution type radiographic screen, while the latter is appropriate for preparing a high-sensitivity type radiographic screen.

Examples of preferred supports include polyethylene terephthalate, clear or blue colored or black colored (e.g., LUMIRROR C, type X30 supplied by Toray Industries, Tokyo, Japan), polyethylene terephthalate filled with  $\text{TiO}_2$  or with  $\text{BaSO}_4$ .

These supports may have thicknesses which may differ depending on the material of the support, and may generally be between 60 and 1000 micron, more preferably between 80 and 500 micron from the standpoint of handling.

The coating procedure of the phosphor layer, useful solvents for the binder of the phosphor containing layer as well as useful dispersing agents, useful plasticizers, useful fillers and subbing or interlayer layer compositions have been described in extenso in the European Patent Application 91/201009.7.

The invention is illustrated by the following examples without however limiting it thereby. All ratios and percentages are by weight unless mentioned otherwise.

## EXAMPLES

### Preparation of X-ray conversion screens

A phosphor coating composition was prepared by intimately mixing the following components as described below:



Gd<sub>2</sub>O<sub>2</sub>S:Tb

polyethyl acrylate (30 % in ethyl acetate)

methyl ethyl ketone

methyl glycol

2-butanone

dispersing agent GAFAC RM 610 (tradename)

ethyl acetate

The green light emitting terbium doped gadolinium oxysulphide phosphor (80 %) was predispersed in a low viscous presolution (20 %) of binder.

The presolution consisted of 7 % by weight of polyethyl acrylate, 18 % of ethyl acetate, 50 % of methyl ethyl ketone, 24.5 % of methyl glycol and 0.5 % of GAFAC RM 610 (tradename). Subsequently, polyethyl acrylate binder and ethyl acetate solvent were added to the phosphor predispersion to obtain a solution with a solid content of 70 %, with 89 % of phosphor with respect to 11 % of binder. Said composition was doctor blade coated onto a subbed 200  $\mu$ m thick polyethylene terephthalate support at a phosphor coverage of 60 g/m<sup>2</sup> and dried. It has to be said that every known phosphor or phosphor mixture, whether conventional or photostimulable, could have been coated as this layer.

#### Preparation of the UV-curable protective topcoat layer

The radiation curable topcoat-layer composition was prepared by mixing in a 60/40 ratio a mixture of prepolymers with the diluent monomer hexane diol diacrylate (HDDA). Said mixture of prepolymers consisted in a 70/30 ratio of (1) an aliphatic polyether-urethane acrylate having per polymer chain 6 acrylic double bonds, an average molecular weight of 1000, and Hoeppler viscosity at 25 DEG C of 100,000 mPa.s], and (2) an aliphatic polyester-urethane acrylate having per polymer chain 3 acrylic double bonds, an average molecular weight of 1500, said pre-polymer being mixed with 15 % of HDDA [Hoeppler viscosity of (2) at 60 DEG C = 30,000 mPa.s].

The photoinitiator DAROCUR 1173 (tradename) was added in a 5 % ratio with respect to the coating composition.

The radiation curable coating composition had a Hoeppler viscosity of 1000 mPa.s at 20 DEG C, the coating temperature.

Actually the coating by screen printing was carried out with a STORK (tradename) printing system PD-IV operating with a cylindrical Stork DLH sieve used as a template and having a circumference of 64 cm (mesh 155, thickness 110 micron, open area 6-8 %, diameter of the circular openings 43-49 micron). The obtained coating thickness  $d$  was 8-10  $\mu$ m and the printing proceeded at a speed of 4 m/min. The doctor blade was made of stainless steel with a length of 20 mm and a thickness of 0.2 mm. Further adjustments of the coating machine were: a pressure of the doctor blade of 6 units, and a height of said doctor blade of 21 units.

#### UV radiation Curing

The applied radiation curable coating composition was cured by UV radiation using a Labcure Unit supplied by Technigraf GmbH, Grävenwiesbach, W. Germany (air cooling, energy output of 80 W/cm, velocity 4 m/min, distance UV source-substrate 11 cm).

A series of screens were made varying in roughness  $R_z$  from 1 to 8  $\mu$ m defined from "perthometer" measurements cited hereinbefore. To obtain said series variations were applied to rheology determining parameters like the pressure and the height of the doctor blade, the amounts and the concentrations of the solvents added to the phosphor predispersion, the squeegee pressure and the coating velocity.

Transport and manipulation characteristics can be simulated making use of a vacuum suction experiment. Principally a rubber sucking-cup is put on the X-ray conversion screen creating underpressure between the sucking-cup and the screen surface by vacuum suction. Experimentally the time can be measured between the moment that the vacuum suction has been ended and the moment that the contact between

the screen and the cup has been broken. Use can be made therefore of the "Automatic Bekk Smoothness Tester, code 131ED" from Büchel-Van Der Korput BV (Veenendaal, Holland), allowing to register the relationship between the contact time  $t$  and the roughness of the screen  $R_z$  as has been illustrated in Fig. 1. Fig. 1 shows that the higher the roughness  $R_z$ , the shorter the contact time is between the screen and the contacting material after vacuum suction, due to the easier migration of air between said contacting materials.

As can be seen from Figure 1 good transport characteristics, linked with shorter contact times measured with the "Automatic Bekk Smoothness Tester" cited hereinbefore, are favoured when the roughness  $R_z$  is increasing from 3 to 8  $\mu\text{m}$  corresponding to a VRd-value defined hereinbefore of at least 0.35.

The overall thickness of 8-10  $\mu\text{m}$  for the protective layer is in favour of image-sharpness.

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**Luminescent article with protective coating and manufacture.****Claims of EP0510754**

1. A luminescent article comprising a self-supporting or supported layer of phosphor particles dispersed in a resin binder having applied thereto a protective coating having an embossed structure.
2. A luminescent article according to claim 1, wherein the protective layer has a layer thickness  $d$  comprised between 1 and 50  $\mu\text{m}$  and an embossed surface roughness  $R_z$  so that the ratio between roughness  $R_z$  and thickness  $d$ , called VRd, is at least 0.35.
3. A luminescent article according to claim 2, wherein said protective layer has a thickness  $d$  comprised between 2 and 30  $\mu\text{m}$ .
4. A luminescent article according to claim 2, wherein said protective layer has a thickness  $d$  comprised between 3 and 25  $\mu\text{m}$ .
5. A luminescent article according to claim 2 to 4 wherein said protective layer is a radiation cured coating.
6. Method of making a luminescent article according to any of claims 1 to 5 comprising the steps of
  - (1) coating onto said phosphor containing layer a liquid radiation-curable composition having at the coating temperature a viscosity of at least 450 mPa.s, measured with a Hoepler viscometer, that does not penetrate for a substantial degree into the phosphor containing layer,
  - (2) providing an embossed structure to the coating, and
  - (3) curing said coating by radiation.
7. Method according to claim 6, wherein said radiation-curable liquid coating composition has a viscosity in the range from 450 to 20,000 mPa.s at 25 DEG C measured with a Hoepler viscometer.
8. Method according to claim 6 or 7, wherein said radiation-curable liquid coating composition is applied by screen-printing.
9. Method according to claim 8, wherein said screen-printing occurs with a rotary screen printing device.
10. Method according to any of claims 6 to 9, wherein the radiation curing proceeds by ultraviolet radiation or electron beam radiation.
11. Method according to any of claims 6 to 10 wherein the roughness  $R_z$  is obtained by passing the screen with uncured or only slightly cured protective coating through the nip of pressure rollers the roller contacting the coating having a micro-relief structure.
12. Method according to any of claims 6 to 10 wherein the roughness  $R_z$  is obtained at the stage of coating by applying the coating composition by means of a gravure roller or screen printing device.

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